Separation Methods Based on Distributions in Discrete Stages (02/02/15)

1. Chemical Separations: The Big Picture
   Classification and comparison of methods

2. Fundamentals of Distribution Separations

3. Separation Methods Based on Distributions in Discrete Stages
   Such as solvent extraction and distillation

4. Introduction to Distribution Separations in chromatographic methods. The plate theory, the rate theory; van Deemter's equation.
Counter-Current Extraction

- [A] = 0.01 M
- [B] = 1 M
- \( V_1 = V_2 = 10 \text{ mL} \)
- \( D_{CA} = 10, \quad D_{CB} = 0.1 \)

Extraction 1

Addition of fresh phases to Both phase 1 and 2

Extraction 2

Separation of phases

Extraction 3
Counter-Current Extraction

[A] = 0.01 M
[B] = 1 M

V₁ = V₂ = 10 mL
Dca = 10, Dcb = 0.1

Extraction 1
Separation of phases

Extraction 2
Addition of fresh phases to Both phase 1 and 2

Total A = 0.909
Total B = 0.091

fA₂₁ = 0.909
fB₂₁ = 0.091

fA₁₂ = 0.008
fB₁₂ = 0.826

Total A = 0.091
Total B = 0.909

fA₁₂ = 0.008
fB₁₂ = 0.826

fA₂N₂ = 0.083
fB₂N₂ = 0.083

fA₁N₂ = 0.083
fB₁N₂ = 0.083
Counter-Current Extraction

Separation of phases

Total A = 0.166
Total B = 0.166

Extraction 3

[A] = 0.01 M
[B] = 1 M
$V_1 = V_2 = 10\ mL$
$D_{cA} = 10$, $D_{cB} = 0.1$
Counter-Current Extraction

\[
f_{A2,2} = 0.826 \\
f_{B2,2} = 0.008 \\
f_{A2N,3} = 0.151 \\
f_{B2N,3} = 0.015 \\
f_{A1N,3} = 0.015 \\
f_{B1N,3} = 0.151 \\
f_{A1,2} = 0.826 \\
f_{B1,2} = 0.008
\]

Results: recovery of A in phase 2 = 0.826 + 0.151 = 0.977 = 97.7%

Final purity of A in phase 2 = \[
\frac{(0.01\text{M}) \times (0.01\text{L}) \times (0.977)}{(0.01\text{M}) \times (0.01\text{L}) \times (0.977) + (1.00\text{ M}) \times (0.01\text{L}) \times (0.023)} = 0.298 = 29.8%
\]

Purification yield = \[
\frac{0.298}{0.0099} = 30
\]

<table>
<thead>
<tr>
<th>One-step</th>
<th>Two-step</th>
<th>Counter-current</th>
</tr>
</thead>
<tbody>
<tr>
<td>Recovery of A in phase 2 = 0.909 = 90.9%</td>
<td>99.2%</td>
<td>97.7%</td>
</tr>
<tr>
<td>Final purity of A in phase 2 = 0.091 (9.1%)</td>
<td>5.4%</td>
<td>29.8%</td>
</tr>
<tr>
<td>Purification yield of A = 9.2</td>
<td>5.45</td>
<td>30</td>
</tr>
</tbody>
</table>
F. Craig Apparatus and Craig Countercurrent distribution

(1) Counter-current extraction are useful in that they improve both the recovery and purification yield of A. However, the technique is time-consuming and tedious to perform.

(2) To overcome these difficulties L. C. Craig developed a device in 1994 to automate this method. Known as the Craig Apparatus, this device uses a series of “separatory funnels” to perform a counter-current extraction. The pattern formed by the movement of a solute through the system is known as a counter-current distribution.
(4) The result of this process is that solutes partition between the phases in each tube, but eventually all travel to the right and off of the apparatus, where they are collected.

(5) Since this system involves both rate and phase separation processes (i.e., distribution of solutions between two phases affecting their rate of travel through the system), The Craig countercurrent distribution is often as a simple model to describe chromatography. In fact, another term often used for countercurrent distribution is countercurrent chromatography (CCC).
H. Theory of Countercurrent distribution:

(1) As in simple extraction, the distribution of A in any tube can be calculated based on its concentration distribution ratio, where

\[
f_{\text{phase}1} = \frac{1}{1 + D_c \frac{V_2}{V_1}} \quad \text{(fraction of A not removed from phase 1)}
\]

\[
f_{\text{phase}2} = 1 - f_{\text{phase}1,1} \quad \text{(fraction of A extracted into phase 2)}
\]

(2) In describing the Craig distribution, the terms \( f_{\text{phase}1} \) and \( f_{\text{phase}2} \) are often replaced with the terms \( q \) and \( p \), where

\[
q = f_{\text{phase}1} = \frac{1}{1 + D_c \frac{V_2}{V_1}}
\]

\[
p = f_{\text{phase}2} = 1 - f_{\text{phase}1,1} = 1 - q
\]

(3) The ratio of \( q/p \) (i.e., the ration of the fraction (or moles) of A in the stationary phase to the fraction (or moles) of A in the mobile phase at equilibrium) is known as the capacity factor \( k' \).

\[
k' = \frac{p}{q} = \frac{\text{mole A}_{\text{mobile phase}}}{\text{moles A}_{\text{stationary phase}}}
\]
(4) The equation for $k = q/p$ may also be rewritten in terms of $p$ and $q$, where

\[ p = \frac{k'}{1 + k'} \]
\[ q = \frac{1}{1+k'} \]

(5) $k$ and concentration distribution ratio ($D_c$) are related by the expression

\[ k' = D_c \frac{V_2}{V_1} \]

In other words, $k'$ is another way to describe the distribution of $A$ between two phase. $D_c$ and $k$ only differ in that $k$ is based on the moles of $A$ present rather than its concentration. For this reason, $k'$ is sometimes referred to as the mass distribution ratio.

(6) The use of $k'$ to describe the distribution of a solute is particularly valuable in situations where the exact volumes of the mobile and stationary phases are not known. One common example of this is on chromatography ($k=1/k'$).

(7) The value of $k'$, or $p$ and $q$, can also be used to describe the distribution of a solute $A$ in the Craig apparatus.
Development of solute distribution in Craig Apparatus

**Extraction 1**

- **Total amount of solute**: $q$
- **Transfer 1**: $p$

**Total amount of solute in each stage**

- $q$
- $p$

**Extraction 2**

- **Total amount of solute**: $q^2$
- **Transfer 1**: $p^2$

**Final distribution of solution**

- $(q+p)$
Extraction 3

Transfer 3

Total amount of solute in each stage

\[ (q+p)^2 \]

\[ (q+p)^3 \]
Development of solute distribution in Craig Apparatus

Transfer 1

\[
\begin{align*}
\text{Distribution of solution} & \quad (q+p) \\
p & \\
q & \\
\end{align*}
\]

Transfer 2

\[
\begin{align*}
\frac{q^2}{q^2} & \\
\frac{qp}{qp} & \\
\frac{p^2}{p^2} & \\
\end{align*}
\]

\[
\begin{align*}
\frac{(q+p)^2}{(q+p)^2} & \\
\frac{q^2}{q^2} & \\
\frac{qp}{qp} & \\
\end{align*}
\]

Transfer 3

\[
\begin{align*}
\frac{qp^2}{qp^2} & \\
\frac{2qp^2}{2qp^2} & \\
\frac{p^3}{p^3} & \\
\end{align*}
\]

\[
\begin{align*}
\frac{q^3}{q^3} & \\
\frac{2q^2p}{2q^2p} & \\
\frac{q^2p}{q^2p} & \\
\end{align*}
\]

\[
\begin{align*}
\frac{(q+p)^3}{(q+p)^3} & \\
\frac{q^3}{q^3} & \\
\frac{2q^2p}{2q^2p} & \\
\frac{q^2p}{q^2p} & \\
\end{align*}
\]
(8) The distribution of A in this system after r transfers is given by the binomial expression of the equation

\[(q + p)^r = 1\]

Where:
\[(q+p)^1 = q + p\]
\[(q+p)^2 = q^2 + 2qp + p^2\]
\[(q+p)^3 = q^3 + 3q^2p + 3qp^2 + p^3, \text{ etc}\]

(9) After given number of transfers (r), the relative amount of A in any tube n is

\[P_{r,n} = \frac{r!}{n!(r-n)!} \frac{p^n q^{r-n}}{n! (r-n)!}\]

Where: \(P_{r,n} = \text{Fraction of A in tube n after transfer r.}\)

Good news: We can get the distribution of solute among Craig tubes (chromatographic column)
Bad news: give no distribution shape and position.

http://www.chem.uoa.gr/Applets/AppletCraig/Appl_Craig2.html
(10) The binomial can be expended as Gaussian distribution when \( n \) larger than 20 (\( r_{pq} > 3 \)).

\[
P_{r,n} = \frac{1}{\sqrt{2\pi} \times \sqrt{r_{pq}}} \ Exp \left[-\left(n-r_p\right)^2/2r_{pq}\right]
\]

Where: \( P_{r,n} \) = Fraction of A in tube \( n \) after transfer \( r \).

(11) The tube containing the largest amount of A (\( n_{max} \)) after \( r \) transfer (peak position):

\[
n_{max} = r_p = r \left[ k'/(1 + k') \right]
\]

(12) The width of the Gaussian distribution function (peak width) is determined by

\[
\sqrt{r_{pq}} = \sigma = \sqrt{r \times k'/(1+k')^2}
\]

(13) By comparing how the position of a “peak’s” maximum and its width change with the number of transfers (or number of equilibria), it becomes clear that the reason that solute become better separated with more transfers is that the distance between their peak maximum is growing faster than their peak widths (i.e. \( n_{max} \propto r \), but \( \sigma \propto \sqrt{r} \)).

This is the fundamental reason why the Craig apparatus and chromatography can be used to separate compounds.
Countercurrent Extraction - Craig Apparatus

A- and B-fractions vs Tube number

Distribution ratios

A: 0.1
B: 3

Eluted A: 0.0%
Eluted B: 0.0%
Transfer: 0

Craig apparatus

Designed by C. E. Efstathiou, Department of Chemistry, University of Athens, GREECE

Countercurrent Extraction - Craig Apparatus

A- and B-fractions vs Tube number

Distribution ratios

A: 0.1
B: 3

Eluted A: 0.0%
Eluted B: 0.0%
Transfer: 1

Craig apparatus

Designed by C. E. Efstathiou, Department of Chemistry, University of Athens, GREECE

Countercurrent Extraction - Craig Apparatus

A- and B-fractions vs Tube number

Distribution ratios

A: 0.1
B: 3

Eluted A: 0.0%
Eluted B: 0.0%
Transfer: 3

Craig apparatus

Designed by C. E. Efstathiou, Department of Chemistry, University of Athens, GREECE

Countercurrent Extraction - Craig Apparatus

A- and B-fractions vs Tube number

Distribution ratios

A: 0.1
B: 3

Eluted A: 0.0%
Eluted B: 0.0%
Transfer: 18

Craig apparatus

Designed by C. E. Efstathiou, Department of Chemistry, University of Athens, GREECE

http://www.chem.uoa.gr/Applets/AppletCraig/AppI_Craig2.html